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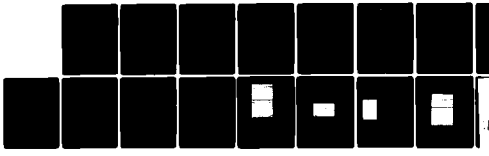

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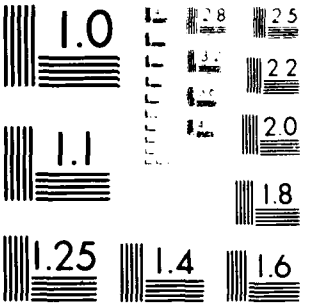

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TECHNICAL REPORT NO. 5

Thermal Diffusivity in Thin Films Measures by Noncontact Single-Ended Pulsed-Laser Induced Thermal Radiometry

by

A. C. Tam and Wing P. Leung

IBM Research Laboratory
San Jose, California 95193

November 22, 1983

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Physics

Research Report

THERMAL DIFFUSIVITY IN THIN FILMS MEASURED BY NONCONTACT SINGLE-ENDED PULSED-LASER-INDUCED THERMAL RADIOMETRY

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Physics

THERMAL DIFFUSIVITY IN THIN FILMS MEASURED BY NONCONTACT SINGLE-ENDED PULSED-LASER-INDUCED THERMAL RADIOMETRY

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ABSTRACT: A pulsed nitrogen laser is used to induce a sharp thermal gradient in a thin film, and the thermal radiation (infrared) transient from the irradiated region is monitored from the same side as the excitation beam (*i.e.*, single-ended detection). We show that this pulsed photothermal radiometry lineshape can be analyzed to provide the thermal diffusivity or thickness of the sample, as well as information on subsurface modifications or the degree of thermal contact with a substrate. We present data for several important classes of films, including metal, polymer and paper (*e.g.*, in currency), and show the important features of the present technique for thin-film characterization, namely nondestructive, fast and remote sensing.

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Thermal diffusivity in materials is traditionally measured[1,2] by contact methods, requiring attachment of electrical and thermocouple leads to a sample. Noncontact methods, using all optical means for excitation and for probing is also possible for a gaseous sample,[3] as well as for a condensed sample.[4] However, most previous techniques are doubled-ended (*i.e.*, measurement devices are on both sides of the sample), making them difficult to use on samples where the backside is inaccessible, *e.g.*, remote, bulky or substrate-mounted. We report here a new noncontact single-ended technique to measure thin-film thermal diffusivity D, if its thickness ℓ is known (actually, it is ℓ^2/D that is measured so that ℓ can also be measured if D is known). We have applied this single-ended "pulsed photothermal radiometry" (PPTR) technique[5] to study metal films, polymer films and paper (*e.g.*, paper currency), and have found that not only can D be measured, but also modifications of surface or substrate conditions can be detected. This indicates that PPTR can be quite useful for remote monitoring of the properties or the adhesion of films, *e.g.*, remote detection of films on solid or on water, and various quality control applications.

Our experimental arrangement is shown in Fig. 1. A pulsed laser of sufficiently short pulse duration τ_L (full width at half maximum) is used to irradiate a surface of a thin-film sample in air. The laser wavelength λ_L is chosen such that the sample is highly opaque at λ_L (*i.e.*, absorption length $<<$sample thickness ℓ) and the pulse width τ_L must be much shorter than the characteristic thermal diffusion time $\tau_D=\ell^2/4D$. We have used a short pulsed ultraviolet laser for this experiment (Molectron UV12 nitrogen laser with $\tau_L=8$ nsec and $\lambda_L=337$ nm). The laser energy emitted is about 1 mJ, and it is suitably attenuated (by up to a factor of 100) so that sample damage does not occur within the irradiated area which is about 0.2 cm^2. The pulsed laser incident on the opaque sample produces a sharp spatial temperature profile f(z) at time t=0, with z being the distance into the sample (z=0 is the

irradiated top surface, and $z=\ell$ is the back surface). This initial temperature profile f(z) causes heat diffusion from the irradiated surface into the sample, thus reducing the top surface temperature $\theta_o(t)$ (above ambient temperature T_o). However, when the heat diffusion "reaches" the back surface, further cooling of the top surface is hindered; *i.e.*, the decay of $\theta_o(t)$ with t characteristically slows down after a critical time t_1, given by

$$t_1 = \ell^2/(4D) \tag{1}$$

We monitor $\theta_o(t)$ by observing the broadband infrared (IR) "grey-body" thermal emission[6-9] from the irradiated surface, using a liquid-nitrogen-cooled HdCdTe detector (New England Research, Model MPP-12-2-J1) sensitive to 8-12 μm radiation with a rise time of 0.5 μsec. For simplicity in the present discussion, we assume that the sample is opaque in the IR (true for the metal films studied). The detected transient IR signal S(t) is

$$S(t) = G\varepsilon\,\sigma([T_o + \theta_o(t)]^4 - T_o^4)\,, \tag{2}$$

or

$$S(t) \approx 4G\varepsilon\,\sigma T_o^3\theta_o(t) \tag{3}$$

where G is a constant depending on the electronic gain and the detector spectral bandwidth, ε is emissivity of the sample surface averaged over the detector bandwidth and σ is the Stefan-Boltzmann constant. Equation (3) is true only if $\theta_o(t)$ is sufficiently small, *e.g.*, not exceeding a few percent of T_o. Under this condition, Eq. (3) indicates that the observed IR radiometry signal S(t) is proportional[6-9] to the top surface temperature $\theta_o(t)$ and should exhibit the characteristic slowing down after a time t_1, as given in Eq. (1).

Quantitative calculation of the transient top and bottom surface temperatures ($\theta_0(t)$ and $\theta_\ell(t)$, respectively) has been given by Parker *et al.*[10] (who extended the work of Carslaw and Jaeger[11]):

$$\left.\begin{matrix}\theta_0(t)\\ \theta_\ell(t)\end{matrix}\right\} = K(1 + 2\sum_{n=1}^{\infty}(\pm 1)^n \exp(-n^2\omega)) \tag{4}$$

where K is a constant independent of time, ω is a dimensionless time given by

$$\omega = \frac{\pi^2}{4}\frac{t}{t_1} \tag{5}$$

with t_1 being given by Eq. (1). Equations (3) and (4) indicate that the PPTR signal S(t) monitoring $\theta_0(t)$ of an isolated homogeneous film has a universal shape once the time scale parameter t_1 is defined; that is, we should be able to fit the signal S(t) by the theoretical form of Eq. (4) by optimizing just one free parameter t_1, which defines the dimensionless time ω. This indicates that (A) the above PPTR method is a new single-ended remote-sensing method to measure either the thermal diffusivity D or the thickness ℓ of a thin film, and (B) we should be able to detect any case of nonisolation or inhomogeneity of a film (*e.g.*, if the film is adhered to a backing instead of being freestanding, or if the film is layered instead of being uniform) by the characteristic deviation of the signal S(t) from the shape of $\theta_0(t)$ in Eq. (4). These conclusions are supported by our experimental results described below. Furthermore, we have also performed the well-known transmission radiometry technique[4,10] (*i.e.*, monitoring $\theta_\ell(t)$ of Eq. (4), as indicated in Fig. 1), obtaining results in agreement with those from PPTR single-ended (Table I).

(a) Metallic Sheets

The observed PPTR signals for five sheets of Type 302 stainless steel shims of thicknesses 12.5, 25, 50, 75 and 125 μm are shown in Fig. 2. The observed signals clearly manifest the shape of $\theta_o(t)$ in Eq. (4). There is an initial sharp decrease in the signal with time and a final "flattening" of the signal after the heat is uniformly distributed across the thickness so that the top surface cools much slower (by heat loss to the surrounding air and heat conduction along the film). As predicted theoretically, the initial sharp decrease is unchanged for different thicknesses, while the magnitude of the final "flattened" signal depends characteristically on the thickness of the sample. A computer program based on Eq. (4) is developed to fit the observed signal; a theoretical fit is shown in Fig. 2c and numerical results of the fit are listed in Table I, where results by other measurement techniques are also listed for comparison. If the back surface of the sample is in contact with a substrate, the shape of the initial sharp signal is unchanged, but the signal at longer times now decays much faster than the isolated film case, as shown in Fig. 3.

(b) Polymer Film

Several types of polymer films have been studied by the PPTR technique, and the results for a teflon film (0.089 mm thick) is indicated in Fig. 4a. The signal for teflon is somewhat broader than the form predicted by Eq. (4) because teflon is not highly opaque in the excitation wavelength (337 nm) nor in the detection wavelength range (8-12 μm).[14] The signal S(t) is now an integral of IR emission from the bulk of the sample instead of only from the top surface as in the metal film case. By taking this fact into account,[15] we have successfully fitted the teflon PPTR signal (Fig. 4b) with the results listed in Table I.

(c) Paper

The observed PPTR signals, when we use a N_2 laser to irradiate 3 mm diameter regions in various dark-green colored regions of U.S. currency bills are indicated in Fig. 5. The signal is highly reproducible when different regions of the bill with about the same amount of coloring is irradiated (see Fig. 5a), showing the high degree of homogeneity of the bill. Also, different bills produce basically the same signal, showing high reproducibility of the bills. Other types of paper give very different signals; for example, the PPTR signals for three "similar" papers (Xerox 4024, Weston bond 25% *cotton fiber and Mead Moistrite* XO-2) are given in Fig. 5b. These samples have approximately the same density and thickness. The results suggest that PPTR can be quite useful as a quality control method for paper and similar materials.

In conclusion, we have made the first quantitative study of the single-ended PPTR technique for noncontact measurement of thermal diffusivities or thickness of an opaque thin film. The examples studied, including metal foils, polymer films and papers, indicate the wide variety of technologically important materials that can be measured by the present noncontact, fast and nondestructive technique.

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TABLE I

Thermal Diffusivities of Some Samples Obtained by Analyzing the Single-ended PPTR Signal, by Analyzing Our Observed Transmission Radiometry Signal as Parker et al. in Ref. 10, and by Other Methods Given in the Literature.

Sample	ℓ (μm)	Thermal Diffusivity D ($10^{-3}cm^2/sec$)		
		Single-ended PPTR	Transmission Radiometry	Other Methods
Type 302 Stainless Steel	12.5	36(8)	32(8)	40.5 (Ref. 12)
	25.0	39(9)	44(9)	
	50.0	36(5)	35(5)	
	125.0	41(6)	(signal too weak)	
Teflon	89.0	0.84	1.0	0.88 (Ref. 13)

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FIGURE CAPTIONS

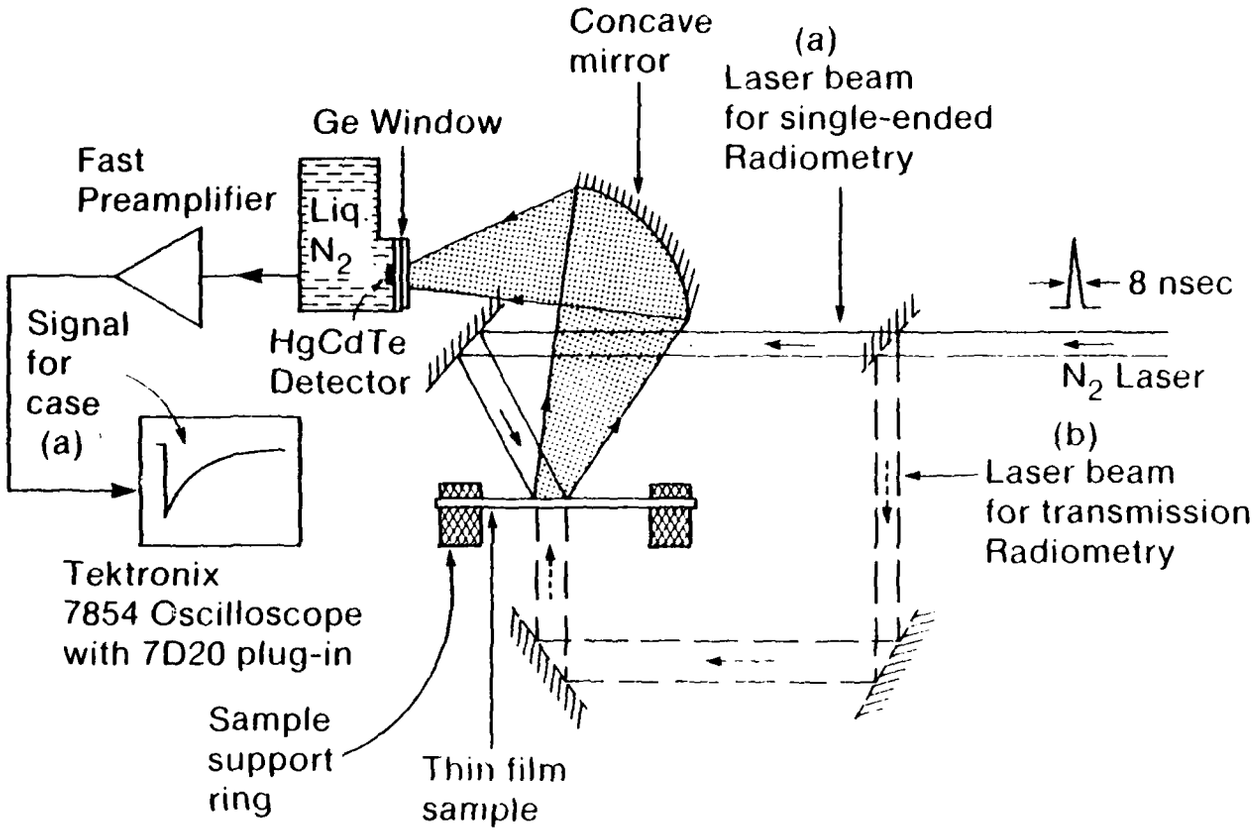
Figure 1. Experimental apparatus for thin-film measurement using PPTR technique. The pulsed N_2 laser beam represented by full lines indicates the present single-ended PPTR technique, while the N_2 laser beam represented by dashed lines (when 3 mirrors represented also by dashed line are installed) indicates the double-ended "transmission" thermal radiometry method used by Parker *et al.* (Ref. 10).

Figure 2. (a) Observed PPTR signals for five type 302 stainless steel sheets of thicknesses 12.5, 25, 50, 75 and 125 μm. Horizontal scale=100 μs/div. (b) The lower trace is the magnified signal for the 12.5 μm thick steel while the upper trace is due to the instrumental scattering effect (scattered N_2 laser beam onto the detector) obtained by putting a glass slide (to block 8-12 μm radiation) in front of the HgCdTe detector. Horizontal scale=2 μs/div. (c) Theoretical fit of the PPTR signal for the 12.5 μm thick stainless steel.

Figure 3. Observed PPTR signal for a free-standing stainless steel sheet of 12.5 μm thickness (lower trace) compared to the same film lying in contact with a quartz substrate (upper trace). Horizontal scale=50 ms/div.

Figure 4. (a) Observed PPTR signal for a teflon film of thickness 89 μm. Horizontal scale=2 ms/div. (b) Theoretical fit of the signal in (a).

Figure 5. (a) Observed PPTR signal when the N_2 laser is used to irradiate a dark-green colored region of a U.S. one dollar bill; (1) and (2) indicates different regions of a new bill and (3) and (4) indicates different regions of an old bill, showing the high degree of reproducibility. Horizontal scale=20 μs/div. (b) Observed PPTR signals for various papers (Xerox 4024, Weston bond 25% cotton fiber and Mead Moistrite OX-2 for top, middle and bottom traces, respectively). Horizontal scale=2 ms/div.



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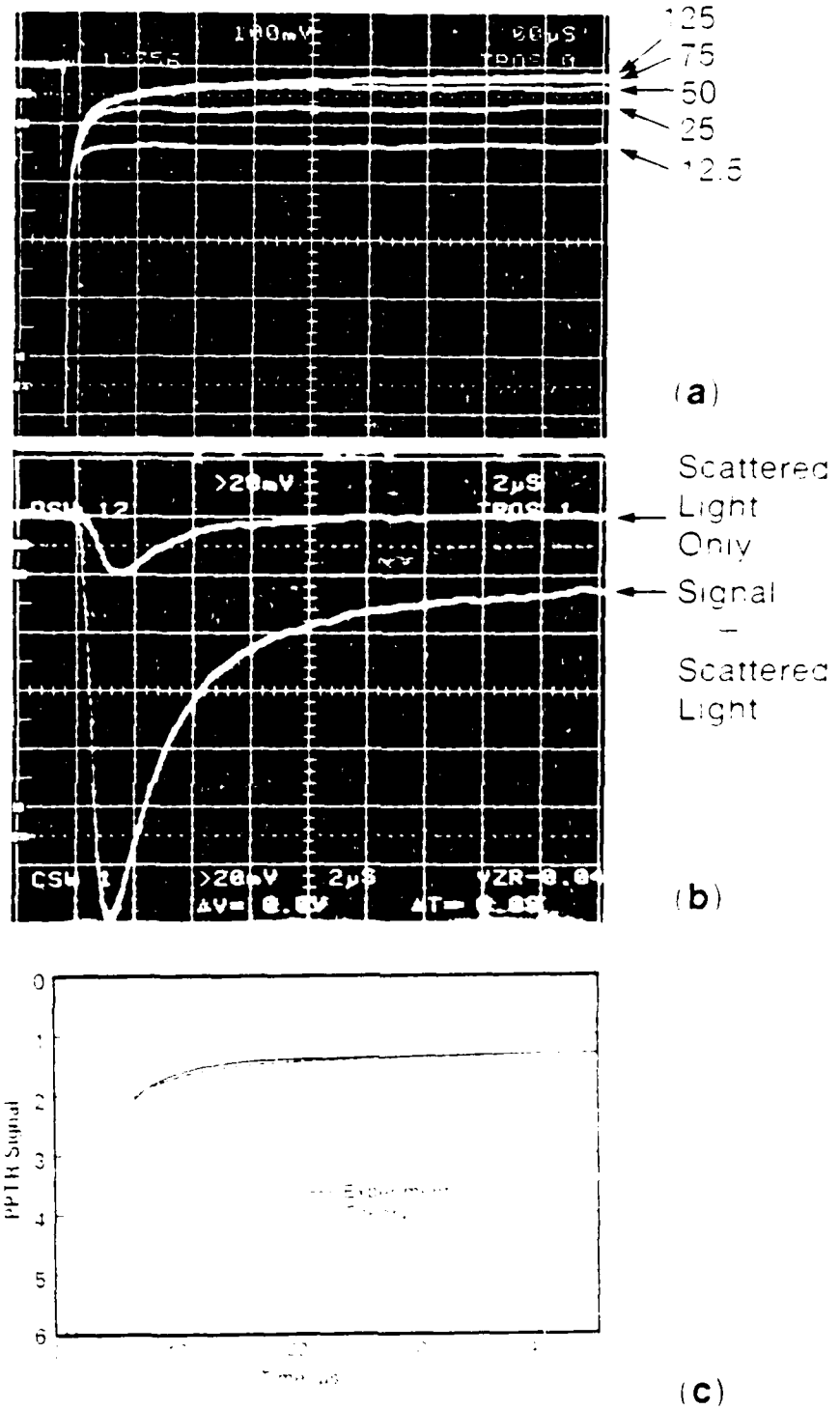

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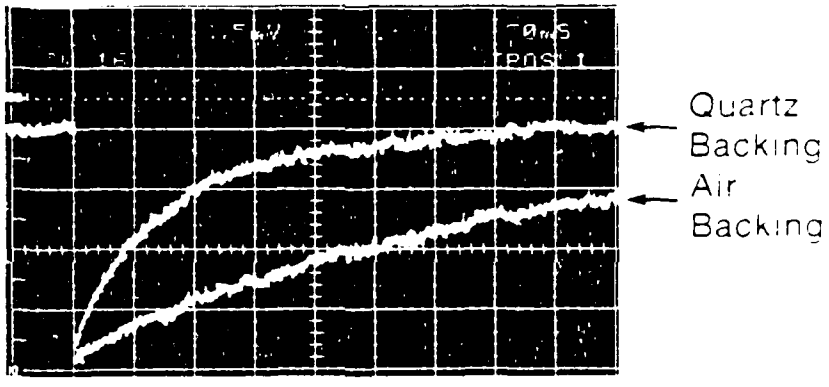

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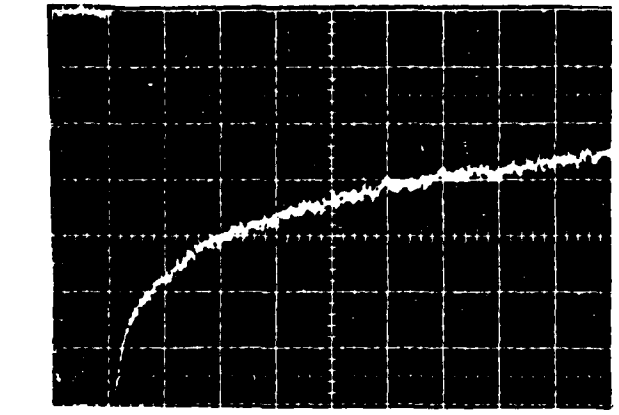

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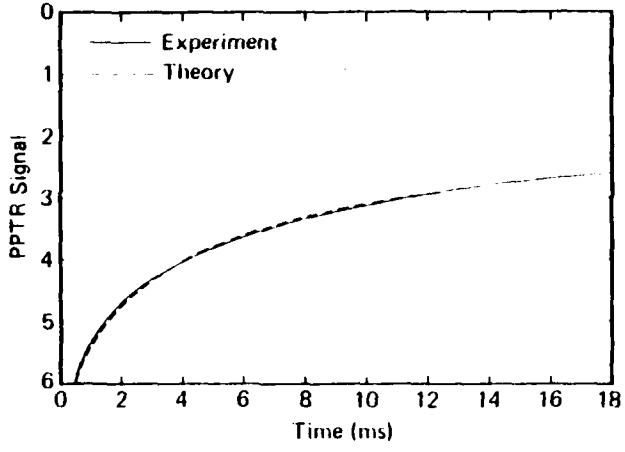

(b)

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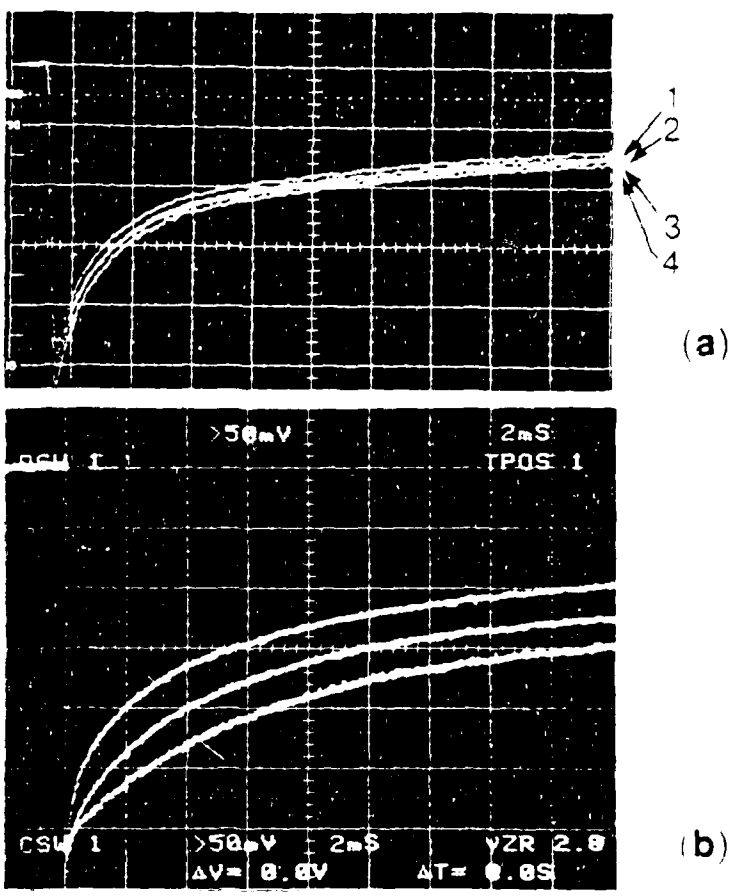

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